

<https://helda.helsinki.fi>

Retention of metal and sulphate ions from acidic mining water by anionic nanofibrillated cellulose

Venäläinen, Salla H.

2017-12-01

Venäläinen , S H & Hartikainen , H 2017 , ' Retention of metal and sulphate ions from acidic mining water by anionic nanofibrillated cellulose ' , The Science of the Total Environment , vol. 599-600 , pp. 1608-1613 . <https://doi.org/10.1016/j.scitotenv.2017.05.009>

<http://hdl.handle.net/10138/307817>

<https://doi.org/10.1016/j.scitotenv.2017.05.009>

cc_by_nc_nd

acceptedVersion

Downloaded from Helda, University of Helsinki institutional repository.

This is an electronic reprint of the original article.

This reprint may differ from the original in pagination and typographic detail.

Please cite the original version.

Retention of metal and sulphate ions from acidic mining water by anionic nanofibrillated cellulose

Salla H. Venäläinen^{a*}

^aUniversity of Helsinki, P.O. Box 27, 00014 University of Helsinki, Finland.

E-mail: salla.venalainen@helsinki.fi

*Corresponding author

Helinä Hartikainen^b

^bUniversity of Helsinki, P.O. Box 27, 00014 University of Helsinki, Finland.

E-mail: helina.hartikainen@helsinki.fi

Abstract

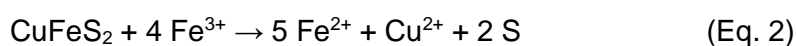
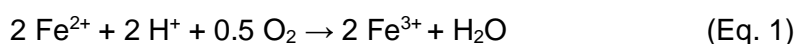
We carried out an adsorption experiment to investigate the ability of anionic nanofibrillated cellulose (NFC) to retain metal and SO_4^{2-} ions from authentic highly acidic (pH 3.2) mining water. Anionic NFC gels of different consistencies (1.1-%, 1.4-% and 1.8-% w/w) were allowed to react for 10 min with mining water, after which NFC-induced changes in the metal and SO_4^{2-} concentrations of the mining water were determined. The sorption capacities of the NFC gels were calculated as the difference between the element concentrations in the untreated and NFC-treated mining water samples. All the NFCs efficiently co-adsorbed both metals and SO_4^{2-} . The retention of metals was concluded to take place through formation of metal-ligand complexes. The reaction between the NFC ligand and the polyvalent cations renders the cellulose nanofibrils positively charged and, thus, able to retain SO_4^{2-} electrostatically. Adsorption capacity of the NFC gels substantially increased upon decreasing DM content as a result of the dilution-induced weakening of the mutual interactions between individual cellulose nanofibrils. This outcome reveals that the dilution of the NFC gel not only increases its purification capacity but also reduces the demand for cellulosic raw material. These results suggest that anionic NFC made of renewable materials serves as an environmentally sound and multifunctional purification agent for acidic multimetal mining waters or AMDs of high ionic strength. Unlike industrial minerals traditionally used to precipitate valuable metals from acidic mining effluents before their permanent disposal from the material cycle, NFC neither requires mining of unrenowable raw materials nor produces inorganic sludges.

Keywords: AMD, purification, metal-ligand complex, co-adsorption, circular economy

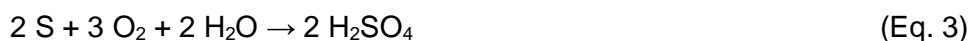
Abbreviations: NFC, Nanofibrillated cellulose; DM, Dry matter; AMD, Acid mine drainage; CN, Cellulose nanomaterial; PLS, Pregnant leaching solution

1. Introduction

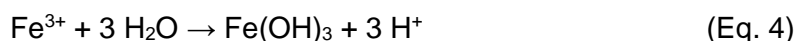
Process waters produced in mining of commercially valuable metals and metalloids as well as runoff waters from e.g. abandoned mines (referred to as acid mine drainage, AMD) are often very acidic and high in solubilised residual elements. If released into the environment, these waters pose serious environmental risks. In addition to acidification and toxicity, they also cause salinisation in the recipient ecosystem (Gray, 1997). The acidity of mining waters originates from the mineralogy of the ores, where the valuable metals typically occur as sulphides. The commercially valuable metal compounds usually occur with other, less valuable metal sulphides such as pyrite (FeS_2) or iron sulphide (FeS) (Johnson, 2014). Extraction of the economically valuable metals takes place through oxidation reactions. Heap bioleaching is currently the most successful technology for the recovery of metals from low-grade sulphide ores (e.g. Bosecker, 1997; Galleguillos *et al.*, 2008; Tao & Dongwei, 2014). In the process, chemolithotrophic acidophilic bacteria (e.g. *Acidothiobacillus ferrooxidans* or *Leptospirillum ferrooxidans*) oxidise ferrous iron (Fe^{2+}) to ferric form (Fe^{3+}) (Eq. 1) (Rawlings, 2001; Rohwerder *et al.*, 2003). Next, the oxidized Fe species acts as an electron acceptor in the oxidation of the desired metal sulphides, e.g. chalcopyrite (CuFeS_2) (Eq. 2, Watling, 2006):



Since Fe^{3+} is highly insoluble at a pH above 2.2 (Lindsay, 1979 p. 130), the microbiologically mediated dissolution of metal sulphides can only take place below it. In addition to external acid commonly fed to the bioleaching system, part of the acid required to keep the process running is generated through the oxidation of elemental sulphur (S), sulphides and reduced inorganic sulphur compounds by means of S-oxidizing bacteria, e.g. *Acidothiobacillus thiooxidans* (Rohwerder *et al.*, 2003; Johnson & Hallberg, 2007). Furthermore, in water, the sulphate produced in the oxidation reaction forms sulphuric acid (H_2SO_4) (Eq. 3) rendering the process water very acidic (Banks *et al.*, 1997; Johnson, 2003; Watling, 2006; Johnson, 2014).



At a pH above 2.2, the oxidized Fe^{3+} species begin to hydrolyse and to precipitate producing additional acidity to the process water (Eq. 4):



In conventional treatment of acidic mining waters, metals not recovered from the pregnant leaching solution (PLS) are precipitated by continuous addition of alkaline materials (Johnson & Hallberg, 2005). Neutralising chemicals are also required in the treatment of flue gases produced in the metal beneficiation. These gases are rich in sulfur dioxide (SO_2) and hydrogen sulphide (H_2S), both of which react with water to produce acids. Commonly used neutralising agents are calcium carbonate (CaCO_3) and its derivatives calcium oxide (CaO) and hydroxide ($\text{Ca}(\text{OH})_2$), magnesium oxide (MgO) and hydroxide ($\text{Mg}(\text{OH})_2$) as well as sodium hydroxide (NaOH) and carbonate (Na_2CO_3) (Coulton *et al.*, 2003; Johnson & Hallberg, 2005). Neutralisation promotes the precipitation of soluble metals as hydroxides. Formation of gypsum (CaSO_4) may also take place when Ca-containing agents are used (Johnson & Hallberg, 2005). The resulting slurry high in precipitated metals will then be pumped into a thickening pond to allow the solids to sediment and to leave the material cycle for good (Salomons, 1995). Highly soluble compounds, such as sodium sulphate (Na_2SO_4) that do not precipitate even at high pH, however, will be released to environment in the final effluent.

In the mining industry, the traditional linear business model (“take & waste”) in which used materials and by-products settle in waste, is not environmentally, ecologically or economically sound. Inefficient use of resources increases the demand for mining of virgin raw materials and, consequently, further consumption of energy and chemicals. Moreover, other wastes generated in mining activities, such as dust, waste rock, tailings, effluents and slurries, will also add to the loading. They also pose a risk of serious environmental hazard in the case of failure of tailings ponds or leakage of toxic solutions to groundwater or surface waters. This kind of an environmental disaster took place in the Talvivaara nickel mine, Finland, in November 2012. A

waste disposal pond containing 5 000 000 m³ of sediment and acidic metal-bearing mining water leaked due to stored water excess. Consequently, 240 000 m³ of environmentally hazardous slurry escaped (Safety Investigation Authority, Finland, 2014).

In the mining industry, novel sustainable technologies are urgently needed for implementing the principles of the circular economy business model, *i.e.* cycling of metals and soluble salts from process water to retain their value as well as to minimize residual wastewater production. Furthermore, new innovative measures are required (a) to reduce the amount of slurries and precipitates generated in mining activities and (b) to meet the challenges related to water balance and quality issues. Insoluble bio-based materials able to retain elements through sorption reactions may provide an environmentally and economically sound alternative for inorganic chemicals or materials made of non-renewable natural resources. In recent years, the use of cellulose-derived nanoscale materials (referred to as nanofibrillated, nanofibrillar or nanofibril celluloses, cellulose nanofibrils, microfibrillated or microfibrillar celluloses, cellulose microfibrils and cellulose nanocrystals, etc.) in water treatment has gained growing interest. Their advantages are the large abundance, low toxicity (e.g. Vartiainen *et al.*, 2011; Alexandrescu *et al.*, 2013), biodegradability (Lin & Dufresene, 2014 and references cited therein) and relatively low cost (Carpenter *et al.*, 2015).

In the synthesis of cellulose nanomaterials (CNs), the raw material (wood, plant, tunicate, algae or bacteria) is pre-treated chemically to remove any matrix materials (e.g. hemicellulose or lignin in wood and plant materials). The purification is followed by isolation of individual cellulose fibres e.g. through mechanical treatment, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation, carboxymethylation, acetylation, acid hydrolysis or enzymatic hydrolysis (Moon *et al.*, 2011; Lavoine *et al.*, 2012). The resulting CNs being 5-100 nm in diameter and 100 nm to several microns in length have the advantage of having a high surface area-to-volume ratio and are highly reactive (Carpenter *et al.*, 2015). Furthermore, the surface properties of CNs can be fairly easily modified by various techniques based on acetylation, silylation, chemical grafting and oxidation

(Lavoine *et al.*, 2012; Kalia *et al.*, 2013) rendering the CN surfaces anionic, cationic, hydrophilic or hydrophobic in nature and, thus, able to retain components of diverse chemical properties.

A number of investigations (reviewed by Carpenter *et al.*, 2015) confirm the ability of anionic CNs to retain various cationic substances from aqueous solutions. Most of the studies have however been carried out with solutions prepared from commercial reagents and at optimised pH (e.g. Yu *et al.*, 2013; Hokkanen *et al.*, 2013; Kardam *et al.*; 2014, Suopajärvi *et al.*, 2015) rather than with more complex authentic industrial water samples.

Our aim was to unravel the utilisation of anionic nanofibrillated cellulose (NFC) in the treatment of authentic acidic mining water. The term NFC used herein refers to CN containing nanofibrils bundles (i.e. cellulose microfibrils) as well as individual nanofibrils liberated from the bundles. Sorption tests determined the capacity of anionic NFC to adsorb Fe, manganese (Mn), aluminium (Al), nickel (Ni), sodium (Na), magnesium (Mg) and sulphate-S from acidic mining water. Furthermore, since CNs are known to swell strongly (Missoum *et al.*, 2013; Liu *et al.*, 2016), we hypothesised that the availability of sorption sites may be related to the hydration rate of the NFC affecting the strength of hydrogen bonding between the individual nanofibrils. Hence, the impact of the consistency of the NFC gel on its capacity to retain metals and S was also tested. To our knowledge, the impact of this factor on the sorption capacity has not been investigated in previous studies.

2. Material and methods

2.1 Mining water

The mining water originated from Terrafame multimetal mine (previously known as Talvivaara Mining Company Plc) located in Sotkamo, Eastern Finland (63°58'30"N 28°00'30"E). The deposit (described in detail by Loukola-Ruskeeniemi & Heino, 1996) is hosted by metamorphosed black schist ore containing Ni (0.23%), copper (Cu, 0.13%), Zn (0.51%) and cobalt (Co, 0.02%) as various sulphide minerals. In addition to the commercially valuable metals, the ore contains Mn (0.3%), Fe (10%), sulphur (S, 9%) carbon (C, 8%) and silica (SiO₂, 50%) (Riekkola-Vanhanen,

2010). The metal extraction is started by heap bioleaching followed by precipitation of the metals through chemical reduction using gaseous H_2S . After recovering the metals from the highly acidic PLS, CaCO_3 and O_2 are added to precipitate most of the Fe as (oxy)hydroxide. Next, $\text{Ca}(\text{OH})_2$ is added to raise the solution pH to 10 to precipitate the remaining metals as hydroxides. The resulting slurries containing metal hydroxides and CaSO_4 are pumped to the nearby gypsum pond. The overflow water from the thickening process is either recycled back to the process or directed to further purification before discharge into the environment (Terrafame, 2017a, 2017b).

The mining water sample we used had been collected after the recovery of metals and preliminary precipitation of Fe. The un-neutralised process water was taken to chemically resemble AMD. It is noteworthy, however, that in the Terrafame mine these process waters are properly purified before their discharge. The water sample was analysed for metals and S (see Section 2.3 for details) and its pH and electrical conductivity were measured (pH meter Consort C6010, conductivity measured with Mettler Toledo T70 titrator). The water was highly acidic (pH 3.2) and rich in dissolved metals and S (Fig. 1) and had a high conductivity of 20 mS cm^{-1} . The process water also contained particulate material identified as precipitated Fe based on its orange colour and the tendency to increase with prolonged exposure to oxygen.

2.2 Nanofibrillated cellulose (NFC)

UPM Kymmene Oyj provided the necessary anionic NFC. Anionisation and fibrillation of the material had been done at the research centre of the manufacturer. In the process, the primary alcohols in cellulose are subjected to TEMPO-mediated oxidation to aldehydes and carboxylic acids using NaClO as a primary oxidant (Saito *et al.*, 2007). The carboxylate content of the anionic pulp, as determined by conductometric titration, was $1 \text{ mmol COOH g}^{-1} \text{ DM}$. Next, the anionic pulp had been dispersed mechanically with water to produce a viscous gel with a dry matter (DM) content of 2.8% (w/w).

For the laboratory experiment, the material was further diluted with Milli-Q[®] water to yield dispersions with a dry matter content of 1.8% (NFC1.8), 1.4% (NFC1.4) and 1.1% (NFC1.1)

determined as weight loss after drying (60°C, 19 h). All the experiments were carried out with the diluted NFCs. The incorporation of the added water into the hydration sphere of the NFC was verified by centrifuging the diluted samples (3600 rpm, 10 min, Hermle Labortechnik Z 513 K). This test confirmed proper association of the added water within all the diluted NFCs with no loose water separating out of any of the samples.

2.3 Experimental design

The capacity of each diluted NFC to retain metals and S was determined in adsorption tests. Therein 10 mL (equivalent to approximately 10 g) of NFC dispersion was injected into 110-mL polypropylene test tubes containing 50 mL aliquots of mining water. Mining water without NFC served as the control. The suspensions were carefully turned over twice, allowed to react for 10 min and passed through a filter paper (Whatman® type 589/3). The control water samples not treated with NFC were prepared according to the same protocol. All filtered solutions collected into plastic bottles were analysed for Fe, Mn, Al, Ni, Na, Mg and S with ICP-OES (Thermo Scientific iCAP 6000). The wavelengths used in the measurement were 396.1 nm for Fe, 293.9 nm for Mn, 238.2 nm for Al, 221.6 nm for Ni, 589.5 nm for Na, 279.5 nm for Mg and 182.0 nm for S. To detect any NFC-induced changes in the acidity of the mining water, pHs of all filtrates were measured (pH meter Consort C6010).

The operation of ICP-OES was controlled by running external standards of known concentrations (prepared from ROMIL PrimAg® Certified Reference Materials, AccuStandard® Accutrace Reference Standard and Perkin Elmer® Pure Instrument Calibration Standard) after every 20 samples. Sorption of metals and S in the different NFC dispersions (mmol kg⁻¹ of DM) was calculated as the difference between the element concentrations (mmol L⁻¹) in the control samples and in the NFC-treated ones. Total sorption of positive charges (Σ [sorbed (+) charges], mol (+) kg⁻¹ DM) was estimated by multiplying the sorbed amount of each cation by its assumed predominant valence at pH 3.2, *i.e.* +2.5 for Fe (average of FeOH²⁺ and Fe³⁺, pK_a 2.19, Lindsay, 1979, p. 130), +3 for Al³⁺ (pK_a 5.02, Lindsay, 1979, p. 36), +2 for Mn²⁺ (pK_a -0.40, Lindsay, 1979, p. 152), +2 for

Ni^{2+} (pK_a 9.86, Mavros *et al.*, 1993), +1 for Na^+ (pK_a 14.2, Lindsay 1979, p. 121), +2 for Mg^{2+} (pK_a 11.45, Lindsay 1979, p. 108). Practically all the negative charges in the solution were assumed to originate from S expected to occur as sulphate SO_4^{2-} (pK_a 1.98) (Lindsay, 1979, p. 284). Since the molarity of SO_4^{2-} equals that of S, the sorption of negative charges (sorbed (-) charges, mol (-) kg^{-1} DM) was calculated by multiplying the sorption of S by 2.

2.4 Statistical analyses

Sorption of each metal and S by the NFCs was calculated as an average of the three replicated samples. A standard deviation (SD) was calculated for sorption of each element. Differences in the sorption capacities between the various NFC dispersions were tested by one-way analysis of variance using Tukey's test for paired comparisons. Statistical analyses were carried out with SPSS 24.0 for Windows. The statistical significance was determined as $p \leq 0.05$.

3. Results

Injecting the NFC gels into the mining water resulted in an instant formation of distinct NFC flocs that tended to resurface. Their approximate size diminished with decreasing DM content in suspension. Treating with the NFCs substantially reduced the turbidity of the mining water as a result of removal of Fe precipitates onto NFCs. The solution phase in the NFC-treated suspensions permeated the filter paper considerably faster than in the control samples. The reaction with the mining water rendered the NFCs orange in colour, particularly in NFC1.1. The filtrates were light yellow but clear with no visible particles. A few hours later, however, Fe particles started to form in the filtrates.

3.1 Retention of cations onto the NFCs differing in their consistencies

NFCs efficiently removed cations from the mining water (Fig. 1). Quantitatively the sorption of the metals followed the order of their concentrations in the initial mining water, decreasing in the order $\text{Fe} > \text{Mg} > \text{Na} > \text{Mn} \gg \text{Al} > \text{Ni}$. Interestingly, when NFC was diluted with water to lower its DM content from 1.8% to 1.4% and 1.1%, the total removal of cations increased from 17.5 mol kg^{-1}

to 23.8 mol kg⁻¹ and 44.1 mol kg⁻¹. Thus, an overall 39% decrease in the DM content of NFC elevated its sorption capacity by 250%. It is noteworthy that the retention did not increase linearly with the lowering DM in the dispersion. Actually, when the DM content was reduced from 1.8% to 1.4% (*i.e.* by 22%), the sorption capacity increased 36%. Upon further decrease from 1.4% to 1.1% (*i.e.* by 21%) the increase was 85%. It is noteworthy that the NFC treatments did not affect the pH of the mining water.

As for the individual cations, when the DM content of NFC was reduced from 1.8% to 1.4%, the sorption of Al, Mn and Na slightly improved, whereas that of Ni, Mg or Fe was not significantly affected (Fig. 1). Interestingly, upon further decrease of the DM to 1.1%, the removal of all cations notably increased. This additional dilution most efficiently promoted the sorption of Mg, Ni and Al.

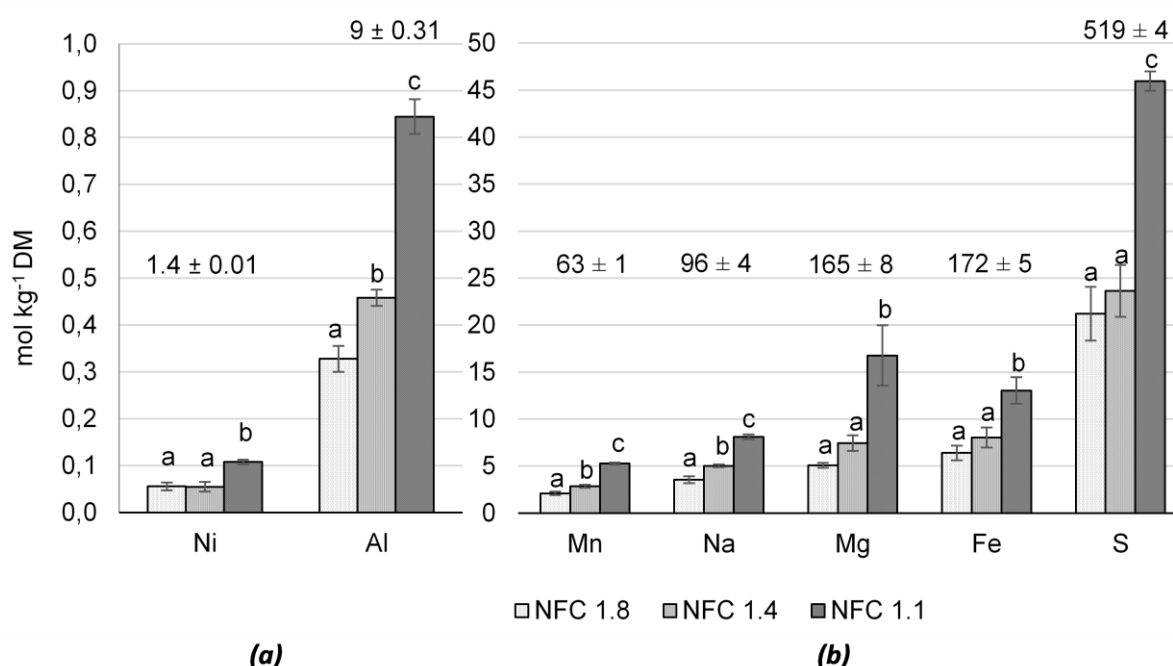


Fig 1. Sorption of (a) Al and Ni and (b) Mn, Na, Mg, Fe and S by NFC1.8, NFC1.4 and NFC1.1 (note the dissimilar scales). Error bars designate the SD of the sorption. Different letters above the columns indicate statistically significant differences ($p \leq 0.05$) in the element-specific sorption by

the NFCs. Initial concentrations of elements in the mining water (mmol L^{-1}) are given above the columns. **(2-column fitting image)**

The main part of the (+) charges retained onto NFCs ($\Sigma[\text{sorbed (+) charges}]$) originated from the Fe species (Fe^{3+} and FeOH^{2+}) and Mg^{2+} (Table 1). Upon dilution of the NFC dispersions the dominance of sorbed Fe species diminished, whereas the relative proportion of sorbed Mg^{2+} increased. As for Mn, Na, Al and Ni, their contribution to the NFCs $\Sigma[\text{sorbed (+) charges}]$ remained practically unchanged regardless of the DM.

3.2 Retention of SO_4^{2-} -S onto the NFCs differing in their consistencies

All NFCs efficiently removed SO_4^{2-} -S from the mining water (Fig. 1). The gradual dilution of the sorbent DM from 1.8% to 1.1% more than doubled the SO_4^{2-} -S retention. Thus, the total increase in the anion sorption capacity was as high as 217%. Interestingly, in the NFC1.8 treatment, the sorbed (-) charges markedly exceeded $\Sigma[\text{sorbed (+) charges}]$ (Table 1). As for the more diluted NFC-treatments, the sorbed (-) charges practically equalled $\Sigma[\text{sorbed (+) charges}]$ (Table 1).

Table 1. Sorption of cation-derived positive charges (mol (+) kg⁻¹), the relative proportion (%) of each cation species on the total sorption of positive charges (Σ [sorbed (+) charges]), and sorption of sulphate-derived negative charges (mol (-) kg⁻¹) in NFCs diluted to contain 1.8, 1.4 and 1.1% of DM. The percentages given for sorbed (-) charges/ Σ [sorbed (+) charges] refer to (+) charges occupied by sulphate.

	NFC1.8		NFC1.4		NFC1.1	
Sorbed (+) charges (mol (+) kg ⁻¹ ± SD)						
Source of charge	% of Σ[sorbed (+) charges]					
Fe ³⁺ , FeOH ²⁺	16.0 ± 2.0	46%	20.1 ± 2.7	43%	32.6 ± 3.6	37%
Mg ²⁺	10.1 ± 0.5	29%	14.9 ± 1.7	32%	33.5 ± 6.4	39%
Mn ²⁺	4.2 ± 0.4	12%	5.7 ± 0.3	12%	10.5 ± 0.3	12%
Na ⁺	3.6 ± 0.4	10%	5.0 ± 0.2	11%	8.1 ± 0.3	9%
Al ³⁺	1.0 ± 0.1	2.8%	1.4 ± 0.1	2.9%	2.5 ± 0.1	2.9%
Ni ²⁺	0.1 ± 0.02	0.3%	0.1 ± 0.02	0.2%	0.2 ± 0.01	0.2%
Σ[sorbed (+) charges]	35.0		47.1		87.5	
Sorbed (-) charges (mol (-) kg ⁻¹)						
SO ₄ ²⁻	42.4		47.3		91.9	
Sorbed (-) charges / Σ[sorbed (+) charges] (%)						
	121%		100%		105%	

4. Discussion

Several previous studies investigated the sorption of various cations from aqueous solutions onto anionic CNs (Table 2). These experiments markedly differ in the cation concentrations and pH of the initial solutions and, consequently, in the sorption capacities obtained (Table 2). A straightforward comparison of various anionic CNs is difficult due to their dissimilar chemical properties depending on their synthetisation method. We, however, can indisputably state that the cation sorption capacities we obtained ($17.5\text{--}44.1\text{ mol kg}^{-1}$) markedly exceeded those previously reported despite a short (10 min) reaction time. The sorption capacity of the NFC was also highly dependent on its DM content, increasing substantially upon decrease from 1.8% to 1.1%. In the previous investigations listed in Table 2, the anionic CNs have been tested at constant DM contents varying from 19% (Hokkanen *et al.*, 2013) to 0.5% (Suopajarvi *et al.*, 2015) and 0.05% (Ma *et al.*, 2012). Yu *et al.* (2013) and Kardam *et al.* (2014) did not provide the DM content.

Table 2. Cation sorption by anionic CNs from aqueous solutions of varying cation concentrations and pH

Reference	Tested CN	Cations	Initial conc. (mmol L ⁻¹)	pH	Max. sorption (mol kg ⁻¹)
Ma <i>et al.</i> (2012)	Ultrafine cellulose nanofibres	UO ₂ ²⁺	0.3-5.6	6.5	0.6
Hokkanen <i>et al.</i> (2013)	Succinic anhydride modified mercerized nanocellulose	Zn ²⁺ , Ni ²⁺ , Cu ²⁺ , Co ²⁺ , Cd ²⁺	0.1-10	5	0.716-1.95
Yu <i>et al.</i> (2013)	Carboxylated cellulose nanocrystals	Pb ²⁺ , Cd ²⁺	1.4-1.8	5.5-6.0	2.2-2.3
Kardam <i>et al.</i> (2014)	Acid hydrolysed nanocellulose fibres	Cd ²⁺ , Pb ²⁺ , Ni ²⁺	0.005-0.85	6.5	0.045-0.15
Suopajärvi <i>et al.</i> (2015)	Sulfonated wheat pulp nanocelluloses	Pb ²⁺	0.24-6.38	5	0.9-1.21

The increase in the cation sorption capacity of the NFC with lowering DM is attributable to the mutual interactions between the nanofibrils being weaker in diluted NFC gels. We hypothesise that when the DM content is high, the spacing between the individual fibrils is narrow. This, in turn, results in stronger interactions between the functional groups of adjacent fibrils through hydrogen bonds, which limits their activity in cation retention. On the other hand, a low DM content favours the hydration of individual nanofibrils. This weakens the hydrogen bonding between the adjacent fibrils and increases their ability to react with cations. The results clearly revealed, however, that the retention capacity does not increase linearly with decreasing DM content. Thus, the optimisation of the DM content is crucial in order to maximize the sorption capacity of NFC.

Yu *et al.* (2013), Hokkanen *et al.* (2013), Kardam *et al.* (2014) and Suopajärvi *et al.* (2015) reported the metal adsorption capacity of CNs to increase with elevated pHs. In our study, the mining water

was considerably more acidic (pH 3.2) than the solutions used in previous studies (5-6.5). Despite this, our cation sorption was significantly higher than that previously reported. The pH dependency of the sorption has previously been attributed to the promoted deprotonation of the functional groups on the CN surface. The subsequent formation of negative surface charge has been assumed to promote the electrostatic attraction between the adsorbent and cations. The authors suggested that at a low pH the adsorption of metals decreases due to enhanced competition between the cations and protons for the same sorption sites. They also proposed that the protonation of the functional groups renders the adsorbent surface positively charged, wherefore the cation retention is hindered by the electrostatic repulsion. These explanations assume the electrostatic sorption to be the principle retention mechanism. The assumption agrees with the finding of Yu *et al.* (2013) who revealed that the adsorbed heavy metals can be replaced by Na⁺ ions in saturated NaCl solution through ion exchange.

It is likely that at low initial concentrations, the retention of cations by anionic CNs takes place through weak electrostatic forces (Ma *et al.*, 2012; Hokkanen *et al.*, 2013; Yu *et al.*, 2013; Kardam *et al.*, 2014; Suopajarvi *et al.*, 2015). This hypothesis agrees with the fact that a low ionic strength contributes to a strong hydration of cations, rendering the interactions between the adsorbent and the cations weak. We, however, propose that instead of an electrostatic adsorption, the principle mechanism of cation retention in the present study was complex or chelate formation. In this type of reaction, a lone electron pair of a ligand (a nucleophile) enters the vacant electron shells of a metal cation (an electrophile), resulting in the formation of a covalent bond between the metal and the ligand. The lone electron pairs required in the reaction were provided by the hydroxyl (OH), aldehyde (COH) and carboxyl (COOH) groups of the cellulose nanofibrils. Contrary to the carboxyl groups (pK_a ~ 5), hydroxyl and aldehyde groups are generally very weak acids (pK_a >> 10) keeping them protonated even at high pH and unable to participate in electrostatic retention of cations. Furthermore, the removal of cations largely exceeded the amount of carboxyl groups in the NFC. This finding supports our hypothesis of the retention mechanism not being electrostatic adsorption.

It is noteworthy that the formation of a metal-ligand complex is based on electron donation rather than on electrostatic attractions. Therefore, it is not only restricted to the deprotonable functional groups. Thus, the reaction may even take place at low pHs. Actually, the high cation retention capacities obtained with the NFCs can be attributable to the large number of functional groups and the pH-independency of metal-complex formation. Even if the electrostatic adsorption was not the principle mechanism of cation retention, however, it is most likely that anionisation of the NFC improves its cation retention properties. This is because electrostatic repulsion between the negatively charged fibrils promotes their individualisation and dispersion when preparing the NFC gel (Isogai *et al.*, 2011). Furthermore, nucleophilicity of ligands increases with increasing negative charge.

The formation of a metal-ligand complex involves the substitution of a water ligand in the co-ordination sphere of a metal cation by the nucleophile. This substitution reaction is favoured by high ionic strength rendering the co-ordination water layer around the cation thinner. A thin hydration sphere provides an easier access for the ligand to the electron shells of the metal cation. Our cation concentration (over 500 mmol L⁻¹) was more than 50-fold compared to that in previous studies (0.005-10 mmol L⁻¹). The high ionic strength of the mining water most likely facilitated the formation of metal-ligand complexes.

Transition metals are able to shift electrons to accommodate ligand configurations, which renders them efficient complexing agents. This property explains the retention of Fe, Mn, Al and Ni by the anionic NFCs from the mining water. Moreover, Fe³⁺ is a particularly strong complexing cation as suggested by the high stability constant of Fe-EDTA complex (log K 25.0, Lindsay, 1979, p. 242). The complex-forming nature of Fe together with its high concentration in the initial solution (172 mmol L⁻¹) explains its pronounced retention by the NFCs. It also supports our theory that the formation of metal-ligand complexes was the principle reaction. Earth and alkaline earth metals, such as Na and Mg, are considered to be weak complex ions as indicated by the low stability constants of Na-EDTA (log K 1.8, Smith & Martell, 1987) and Mg-EDTA (log K 8.83, Lindsay, 1979, p. 242). According to mass action law, however, at high concentrations the weakly complexing

cations may overcome the theoretical tendencies determined by the stability constants. Thus, the high initial concentration of Mg (165 mmol L^{-1}) may partly explain its rather efficient retention from the mining water.

Furthermore, our results revealed that the anionic NFCs were not only able to retain cations but also showed a substantial retention of SO_4^{2-} -anions. In fact, the total sorption of negative charges by the NFCs equalled or even exceeded that of the positive charges. To the best of our knowledge, no previous data is available on the simultaneous sorption of cations and anions by anionic CNs. The surprising finding of the substantial retention of anions by the anionic NFC is supported by our theory. Unlike electrostatic adsorption, the formation of a metal-ligand complex is not based on the neutralisation of negative surface charges with positively charged cations. Thus, the formation of a complex between a divalent or trivalent cation, such as Fe^{3+} , and the anionic ligand (NFC^-) may have rendered the net charge of the NFC surface positive (e.g. FeNFC^{2+}). The pH-independent surplus (+) charge formed on the NFC enables the retention of anions through electrostatic forces, which may explain the retention of SO_4^{2-} . The SO_4^{2-} species being a conjugate anion of the rather acidic HSO_4^- (pK_a 1.98, Lindsay 1979, p. 284), renders SO_4^{2-} a weak base in nature, prone to be retained by electrostatic forces rather than by complex formation. The proportion of sorbed (-) charges to Σ [sorbed (+) charges] was particularly high (121%) in the NFC1.8, where the estimated contribution of Fe to Σ [sorbed (+) charges] was most pronounced (46%). This finding suggests that most of the surplus (+) charge contributing to the sorption of SO_4^{2-} originated from Fe.

Even though the retention of Na is considered rather unlikely due to its high ionic potential, we found that NFCs removed substantial amounts of Na from the mining water. This outcome may be attributable to the abundance of SO_4^{2-} able to form a weak complex with Na. It is possible that at a high initial Na concentration (96 mmol L^{-1}) and high ionic strength, the NaSO_4^- complex was retained electrostatically onto positively charged sites formed in the prior retention of cations.

5. Conclusions

The sorption experiments reveal that anionic NFC is able to retain quickly, efficiently and simultaneously both cations (Fe, Al, Mn, Ni, Mg and Na) and anions (SO_4^{2-}) from authentic acidic mining water. Hence, it may serve as an efficient and multifunctional purification agent in the treatment of acidic multimetal process waters or AMD. The retention of cations by anionic CNs was previously suggested to take place primarily through electrostatic adsorption between deprotonated adsorbent surfaces and positively charged ions. We, however, assume that at high ionic strength the retention of cations takes place through formation of metal-ligand complexes between the cations and the insoluble cellulose nanofibrils. The subsequent formation of net positive charge on the adsorbent surface enables the electrostatic adsorption of SO_4^{2-} . As opposed to electrostatic adsorption of cations, the formation of a metal-ligand complex has the advantage of taking place regardless of pH, rendering the applicability of NFC to the treatment of acidic process waters or AMD superior.

Furthermore, the ability of anionic NFC to function even at a low pH most likely improves the degree of metal recovery, because the metals in the solution will remain as free cations most susceptible to retention by the anionic NFC. In addition, the capacity of the anionic NFC to retain cations and anions can be substantially elevated by decreasing the DM content of the NFC gel. This improves the efficiency of the sorbent while decreasing the demand for raw material. The only restriction is that, to avoid surplus water, all water used in the dilution of the sorbent gel should be retained by the NFC fibrils. The organic nature of the NFC enables the incineration of the used cellulose nanomaterial to carbon dioxide (CO_2) and H_2O and, subsequently, the recycling of the metals and SO_4^{2-} remaining in the ashes. Recovery of the retained elements through chemical regeneration of the NFC may also be possible. Contrary to the chemical precipitation of the valuable metals as insoluble hydroxides and their subsequent discarding, the purification of mining waters by means of renewable materials is in harmony with the principles of the circular economy business model.

Acknowledgements

We thank UPJ Kymmene Oyj for preparing and providing the cellulose nanomaterial for this research and Terrafame Group Ltd. for the process water samples. This study was financially supported by Maj and Tor Nessling Foundation, K.H. Renlund Foundation and Maa- ja vesitekniiikan tuki ry.

References

- Alexandrescu, L., Syverud, K., Gatti, A. & Chinga-Carrasco, G. 2013. Cytotoxicity tests of cellulose nanofibril-based structures. *Cellulose* 20: 1765—1775.
- Banks, D., Younger, P.L., Arnesen, R-T., Iversen, I.R. & Banks, S.P. 1997. Mine-water chemistry: the good, the bad and the ugly. *Environ. Geol.* 32: 157—174.
- Bosecker, K. 1997. Bioleaching: Metal solubilization by micro-organisms. *FEMS Microbiol. Rev.* 20: 591—604.
- Carpenter, A.W., de Lannoy, C-F. & Wiesner, M.R. 2015. Cellulose nanomaterials in water treatment technologies. *Environ. Sci. Technol.* 49: 5277—5287.
- Coulton, R., Bullen, C. & Hallet, C. 2003. The design and optimisation of active mine water treatment plants. *Land Contam. Reclamat.* 11: 273—279.
- Galleguillos, P., Remonsellez, F., Galleguillos, F., Guiliani, N., Castillo, D. & Demergasso, C. 2008. Identification of differentially expressed genes in an industrial bioleaching heap processing low-grade copper sulphide ore elucidated by RNA arbitrarily primed polymerase chain reaction. *Hydrometallurgy* 94: 148—154.
- Gray, N.F., 1997. Environmental impact and remediation of acid mine drainage: a management problem. *Environ. Geol.* 30: 62—71.

- Hokkanen, S., Repo, E. & Sillanpää, M. 2013. Removal of heavy metals from aqueous solutions by succinic anhydride modified mercerized nanocellulose. *Chem. Eng. J.* 223: 40—47.
- Isogai, A., Saito, T. & Fukuzumi, H. 2011. TEMPO-oxidized cellulose nanofibres. *Nanoscale* 3: 71—85.
- Johnson, D.B. 2003. Chemical and microbiological characteristics of mineral spoils and drainage water at abandoned coal and metal mines. *Water, Air, Soil Pollut.: Focus* 3: 47—66.
- Johnson, D.B. 2014. Recent developments in microbiological approaches for securing mine wastes and for recovering metals from mine waters. *Minerals* 4: 279—292.
- Johnson, D.B. & Hallberg, K.B. 2005. Acid mine drainage remediation options: a review. *Sci. Total. Environ.* 338: 3—14.
- Johnson D.B. & Hallberg K.B. 2007. Techniques for detecting and identifying acidophilic mineral-oxidizing microorganisms. In: Rawlings D.E., Johnson D.B., (Eds.). *Bio mining*. Springer; 2007. pp. 237–261.
- Kalia, S., Boufi, S., Celli, A. & Kango, S. 2013. Nanofibrillated cellulose: surface modification and potential applications. *Colloid Polym. Sci.* 292: 5—31.
- Kardam, A., Rohit, K, Shalini, R., Srivastava, S. & Srivastava, M.M. 2014. Nanocellulose fibers for biosorption of cadmium, nickel, and lead ions from aqueous solution. *Clean Technol. Envir.* 16: 385—393.
- Lavoine, N., Desloges, I., Dufresne, A. & Bras, J. 2012. Microfibrillated cellulose – Its barrier properties and applications in cellulosic materials: A review. *Carbohydr. Polym.* 90: 735—764.
- Lin, N. & Dufresene, A. 2014. Nanocellulose in biomedicine: Current status and future prospect. *Eur. Polym. J.* 59: 302—325.
- Lindsay, W.L. 1979. *Chemical equilibria in soils*. John Wiley & Sons, Inc, USA. 449p.

- Liu, J., Chinga-Carrasco, G., Cheng, F., Xu, W., Willför, S., Syverud, K. & Xu, C. 2016. Hemicellulose-reinforced nanocellulose hydrogels for wound healing application. *Cellulose* 23: 3129—3143.
- Loukola-Ruskeeniemi, K. & Heino, T. 1996. Geochemistry and genesis of the black shale-hosted Ni–Cu–Zn deposit at Talvivaara, Finland. *Econ. Geol.* 91: 80—110.
- Ma, H., Hsiao, B.S. & Chu, B. 2012. Ultrafine cellulose nanofibers as efficient adsorbents for removal of UO_2^{2+} in water. *ACS Macro Lett.* 1: 213—216.
- Mavros, P., Zoupoulis, A.I. & Lazaridis, N.K. 1993. Removal of metal ions from wastewaters. The case of nickel. *Environ. Technol.* 14: 83—91.
- Missoum, K., Belgacem, M.N. & Bras, J. 2013. Nanofibrillated cellulose surface modification: A review. *Materials* 6: 1745—1766.
- Moon, R.J., Martini, A., Nairn, J., Simonsen, J. & Youngblood, J. 2011. Cellulose nanomaterials review: structure, properties and nanocomposites. *Chem. Soc. Rev.* 40: 3941—3994.
- Riekkola-Vanhanen, 2010. Talvivaara Sotkamo mine – Bioleaching of a polymetallic nickel ore in subarctic climate. *Nova Biotechnologica* 10: 7—14.
- Rawlings, D.E. 2001. The molecular genetics of *Thiobacillus ferrooxidans* and other mesophilic, acidophilic, chemolithotrophic, iron- or sulfur-oxidizing bacteria. *Hydrometallurgy* 59: 187—201.
- Rohwerder, T., Gehrke, T., Kinzler, K. & Sand, W. 2003. Bioleaching review Part A: Progress in bioleaching: fundamentals and mechanisms of bacterial metal sulfide oxidation. *Appl. Microbiol. Biotechnol.* 63: 239—248.
- Safety Investigation Authority, Finland 2014. Environmental accident at the Talvivaara mine in November 2012. Safety Investigation Report 5/2014. Available from: http://www.turvallisuustutkinta.fi/material/attachments/otkes/tutkintaselostukset/fi/muutonnettomuudet/2012/k2wFN7MMJ/Y2012-03_Tutkintaselostus.pdf. Last accessed 18/04/2017.

- Saito, T., Kimura, S., Nishiyama, Y. & Isogai, A., 2007. Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose. *Biomacromolecules* 8: 2485—2491.
- Salomons, W. 1995. Environmental impact of metals derived from mining activities: processes, predictions, prevention. *J. Geochem. Explor.* 52: 5—23.
- Smith, R.M. & Martell, A.E. 1987. Critical stability constants, enthalpies and entropies for the formation of metal complexes of aminopolycarboxylic acids and carboxylic acids. *Sci. Total Environ.* 64: 125—147.
- Suopajärvi, T., Liimatainen, H., Karjalainen, M., Upola, H. & Niinimäki, J. 2015. Lead adsorption with sulfonated wheat pulp nanocelluloses. *J. Water Process Eng.* 5: 136—142.
- Tao, H. & Dongwei, L. 2014. Presentation on mechanisms and applications of chalcopyrite and pyrite bioleaching in biohydrometallurgy – a presentation. *Biotechnology Reports* 4: 107—119.
- Terrafame, 2017a. Water purification. Available from:
<https://www.terrafame.com/environment/environment-water-management/water-purification.html>.
 Last accessed 24/4/2017.
- Terrafame, 2017b. Environmental monitoring report 2016. In Finnish. Available from:
https://www.terrafame.fi/media/ymparistoraportit/2016/vuosiraportti2016_osa3_vesipaastojen_tarkkailu.pdf. Last accessed 24/4/2017.
- Vartiainen, J., Pöhler, T., Sirola, K., Pylkkänen, L., Alenius, H., Hokkinen, J., Tapper, U., Lahtinen, P., Kapanen, A., Putkisto, K., Hiekkataipale, P., Eronen, P., Ruokolainen, J. & Laukkanen, A. 2011. Health and environmental safety aspects of friction grinding and spray drying of microfibrillated cellulose. *Cellulose* 18: 775—786.
- Watling, H.R. 2006. The bioleaching of sulphide minerals with emphasis on copper sulphides — A review. *Hydrometallurgy* 84: 81—108.
- Yu, X., Tong, S., Ge, M., Wu, L., Zuo, J., Cao, C. & Song, W. 2013. Adsorption of heavy metal ions from aqueous solutions by carboxylated cellulose nanocrystals. *J. Environ. Sci.* 25: 933—943.